

# First-principle studies of the spin-orbit and the Dzyaloshinskii-Moriya interactions in the $\{\text{Cu}_3\}$ single-molecule magnet

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Frustrated triangular molecule magnets such as  $\{\text{Cu}_3\}$  are characterized by two degenerate  $S=1/2$  ground-states with opposite chirality. Recently it has been proposed theoretically [PRL **101**, 217201 (2008)] and verified by *ab-initio* calculations [PRB **82**, 155446 (2010)] that an external electric field can efficiently couple these two chiral spin states, even in the absence of spin-orbit interaction (SOI). The SOI is nevertheless important, since it introduces a splitting in the ground-state manifold via the Dzyaloshinskii-Moriya interaction. In this paper we present a theoretical study of the effect of the SOI on the chiral states within spin density functional theory. We employ a recently-introduced Hubbard model approach to elucidate the connection between the SOI and the Dzyaloshinskii-Moriya interaction. This allows us to express the Dzyaloshinskii-Moriya interaction constant  $D$  in terms of the microscopic Hubbard model parameters, which we calculate from first-principles. The small splitting that we find for the  $\{\text{Cu}_3\}$  chiral state energies ( $\Delta \approx 0.02$  meV) is consistent with experimental results. The Hubbard model approach adopted here also yields a better estimate of the isotropic exchange constant than the ones obtained by comparing total energies of different spin configurations. The method used here for calculating the DM interaction unmasks its simple fundamental origin which is the off-diagonal spin-orbit interaction between the generally multireference vacuum state and single-electron excitations out of those states

## I. INTRODUCTION

In the last twenty years single-molecule magnets (SMMs) have been widely studied both for their fundamental physical properties<sup>1</sup>, and for possible applications in magnetic storage and quantum information.<sup>2,3</sup> Unlike traditional bulk magnetic materials, molecular magnetic materials can be magnetized in a magnetic field without any interaction between the individual molecules. This magnetization is a property of the molecules themselves. The magnetization occurs because of the large ground-state spin and the large easy-axis magnetic anisotropy barrier separating spin-up and the spin-down states. In principle it is possible to store and manipulate information in one SMM. Furthermore the two quantum states representing the two possible spin orientations can be used to build a quantum qubit. Whether used as classical magnetic storage units or as quantum coherent elements, the crucial requirement in both cases is the ability to control and manipulate the magnetic states of the SMM in an efficient way. Manipulation by magnetic fields is straightforward but, in practice, cannot be realized with molecular-size spatial resolution and at fast temporal scales. Unlike magnetic fields, electric fields are easy to produce, quickly switched and can be applied locally at the nano and molecular scale. Therefore manipulation of the properties of

SMMs by external electric fields is an attractive and promising alternative.<sup>4</sup>

Although electric fields do not directly couple to spins, electric manipulation of the spin states is possible indirectly via spin-orbit coupling. This requires the presence of a strong spin-orbit coupling such that the electric field can effectively flip the spin states by acting on the orbital part of the spin-orbitals. When SMMs are involved, this is not the most efficient mechanism, since the relative strength of spin-orbit interaction scales like the volume of the molecule.

Recently, a different mechanism of spin-electric coupling in antiferromagnetic SMMs, characterized by lack of inversion symmetry and spin frustration, has been proposed.<sup>4</sup> The best example of such a system is a triangular spin  $s = 1/2$  ring with antiferromagnetic coupling, realized for example in the  $\{\text{Cu}_3\}$  SMM. The low energy physics of this system can be described by a three-site spin  $s = 1/2$  Heisenberg Hamiltonian whose ground-state manifold is composed of two degenerate (total) spin  $S = 1/2$  doublets, with wave functions represented by

$$|\chi_{\pm}, S_z = +\frac{1}{2}\rangle = \frac{1}{\sqrt{3}}(|\downarrow\uparrow\uparrow\rangle + \epsilon_{\pm}|\uparrow\downarrow\uparrow\rangle + \epsilon_{\mp}|\uparrow\uparrow\downarrow\rangle), \quad (1)$$

$$|\chi_{\pm}, S_z = -\frac{1}{2}\rangle = \frac{1}{\sqrt{3}}(|\uparrow\downarrow\downarrow\rangle + \epsilon_{\pm}|\downarrow\uparrow\downarrow\rangle + \epsilon_{\mp}|\downarrow\downarrow\uparrow\rangle), \quad (2)$$

where the many-body states  $|\sigma_1\sigma_2\sigma_3\rangle$  are products of spin-orbital states  $\sigma_i = (\uparrow, \downarrow)$ ,  $i = 1, 2, 3$  localized on the three magnetic ions of the molecules, and  $\epsilon_{\pm} = \exp(\pm 2\pi i/3)$ . The four states  $|\chi_{\pm}, S_z = \pm 1/2\rangle$  in Eqs. (1), (2) are labeled by the eigenvalues  $S_z = \pm 1/2$  of the  $z$ -component of the total spin, and by the chirality quantum number  $\chi_{\pm} = \pm 1$ , that is, the eigenvalues of the chiral operator

$$C_z = \frac{4}{\sqrt{3}} \mathbf{s}_1 \cdot \mathbf{s}_2 \times \mathbf{s}_3. \quad (3)$$

An electric field couples to the SMM through  $e\mathbf{E} \cdot \mathbf{R}$ , where  $e$  is the electron charge and  $\mathbf{R} = \sum_{i=1}^3 \mathbf{r}_i$ . The two spin-orbital states  $|\chi_{\pm}, S_z\rangle$ , characterized by opposite chirality and equal spin projection, form the basis of a two-dimensional  $E'$  irreducible representation of  $D_{3h}$ . General group theory arguments then guarantee that the matrix elements,  $e\langle\chi_{+1}, S_z|X_-|\chi_{-1}, S_z\rangle = e\langle\chi_{-1}, S_z|X_+|\chi_{+1}, S_z\rangle = 2id \neq 0$ , where  $X_{\pm} \equiv \pm X + iY$  are the in-plane components of  $\mathbf{R}$ , which also transform as the two-dimensional irreducible representation  $E'$ . Here  $d$  is a real number that is referred to as spin electric-dipole coupling. It follows that, due to these non-zero matrix elements, an electric field can cause transitions between two ground state wavefunctions of opposite chirality but with same  $S_z$ .

The observation of such electric-field induced transitions from one chiral state to another requires that the degeneracies between these states be lifted. The anisotropic Dzyaloshinskii-Moriya (DM) interaction plays a crucial role in that, it provides one possible mechanism that lifts the degeneracies between states of different chirality without mixing them, as shown in Fig. 1. More in general, the presence of DM interaction provides a mechanism to control the size of quantum entanglement in magnetic trimers as a function of the temperature and external magnetic field<sup>5</sup>. Experimentally the DM-induced splitting in  $\{\text{Cu}_3\}$  is estimated to be small (approximately 0.5 K<sup>6</sup>).

Recently<sup>7</sup> we have investigated the details of the electronic properties of the  $\{\text{Cu}_3\}$  SMM, which is one of the most promising triangular spin 1/2 molecules where the spin-electric effect can be realized. In particular, we introduced a scheme to evaluate the strength of spin electric-dipole coupling  $d$  using *ab-initio* methods. However, the value of the anisotropic DM-exchange constant interaction, which is responsible of the GS zero-field splitting, has not yet been calculated. The purpose of this work is to calculate this splitting by *ab-initio*

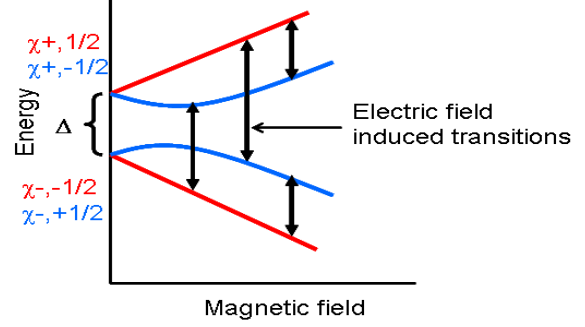


FIG. 1: (Color online) Schematic diagram of electric-field-induced transitions between states of different chirality belonging to the spin  $S = 1/2$  ground-state manifold of a triangular antiferromagnet.  $\Delta$  represents zero-field splitting of the chiral states due to Dzyaloshinskii-Moriya interaction.

methods. In order to achieve this goal, we analyze the microscopic origin of the DM interaction via a Hubbard model approach in the presence of spin-orbit integration, which is the correct minimal model to describe both spin and charge fluctuations of these strongly correlated electron systems. At half-filling and in the large Hubbard  $U$  limit, spin-dependent virtual hopping processes, induced by the spin-orbit interaction, give rise to an anisotropic exchange interaction.<sup>8</sup> There is a close analogy with the isotropic Heisenberg exchange interaction obtained in second-order perturbation theory in the spin-independent hopping perturbation. Beside elucidating the physical mechanism leading to the anisotropic DM exchange interaction, this approach provides a very convenient prescription on how to extract the DM exchange constant from first-principle calculations, which we have carried out for  $\{\text{Cu}_3\}$ .

This paper is organized as follows. In Sec. II A we discuss the general properties of the DM interaction. The Hubbard model approach for calculating DM vector, adopted in this work, is discussed in Sec. II B. In Sec. III we discuss details of extracting Hubbard model parameters from our *ab-initio* calculations. In Sec. III D we discuss other methods that are usually employed for calculating the DM vector. Finally in Sec. IV we present a summary of our work.

## II. THE DZYALOSHINSKII-MORIYA INTERACTION IN FRUSTRATED ANTIFERROMAGNETIC SPIN RINGS

### A. General properties of the DM interaction

The Dzyaloshinskii-Moriya (DM) interaction is an anisotropic exchange interaction resulting from the interplay of the Coulomb interaction and the spin-orbit coupling in systems of low crystal symmetry. The DM interaction is an important effect for many magnetic systems and plays a crucial role in determining the zero-field splitting of energy levels. An anisotropic exchange interaction of the form

$$\mathbf{D}_{12} \cdot \mathbf{S}_1 \times \mathbf{S}_2, \quad (4)$$

which is linear in the spin-orbit interaction, was first put forward by Dzyaloshinskii on the basis of symmetry considerations.<sup>9</sup> Later Moriya<sup>10,11</sup> provided a mechanism for this interaction by extending Anderson's theory of superexchange<sup>12</sup> to include the effect of spin-orbit coupling. Let us consider for simplicity two "magnetic ions",  $\mathbf{R}$  and  $\mathbf{R}'$ , each occupied by a single electron in the ground state. Second-order perturbation theory in the hopping Hamiltonian  $H_t$  coupling the two sites gives rise to an isotropic antiferromagnetic interaction with exchange constant  $J = 2t_{\mathbf{R}\mathbf{R}'}^2/U$ , where  $t_{\mathbf{R}\mathbf{R}'}$  is a spin-independent hopping integral and  $U$  is the energy required to transfer an electron from  $\mathbf{R}$  to  $\mathbf{R}'$ . When spin-orbit interaction  $H_{\text{SOI}}$  is included, similar second-order processes can generate an anisotropic exchange interaction in the form of Eq. (4), with  $D \sim t_{\mathbf{R}\mathbf{R}'}b_{\mathbf{R}\mathbf{R}'}/U$  where  $b_{\mathbf{R}\mathbf{R}'}$  is a SOI-induced or SOI-dependent hopping integral. To lowest-order,  $b_{\mathbf{R}\mathbf{R}'}$  is just the matrix elements of the  $H_{\text{SOI}}$  between two orbitals localized at  $\mathbf{R}$  and  $\mathbf{R}'$ . This is the dominant contribution to  $D$ . In case that at each site more than one orbital  $|\mathbf{R}, \mu\rangle$ ,  $\mu = 1, 2, \dots$  plays a role, higher-order terms such as  $b_{\mathbf{R}\mathbf{R}'} = t_{\mathbf{R}\mathbf{R}'}\langle \mathbf{R}, \mu | H_{\text{SOI}} | \mathbf{R}', \mu' \rangle / \Delta E_{\mu, \mu'}$  are possible, making the corresponding  $D$  effectively a third-order coupling in the perturbations  $H_t$  and  $H_{\text{SOI}}$ . It turns out that  $D \simeq (\Delta g/g)$ , where  $g$  is the free-electron gyromagnetic ratio and  $\Delta g$  the deviation from  $g$  induced by SOI.<sup>11</sup>

As shown by Moriya, other terms linear in the SOI contribute to the anisotropic exchange of the form of Eq. (4). The second most important contribution is also a second-order term resulting from SOI and *direct* inter-atomic exchange interaction  $J^{\text{ex}}(\mathbf{R}, \mathbf{R}')$ . In antiferromagnetic crystals this term is  $J^{\text{ex}}(\mathbf{R}, \mathbf{R}')/J$  times smaller than the second-order contribution proportional to  $t_{\mathbf{R}\mathbf{R}'}b_{\mathbf{R}\mathbf{R}'}$ . Finally, third-order contributions to  $D$  include the hopping

terms twice and the intra-atomic exchange constant  $J_0$ . They are  $J_0/U$  smaller than second-order terms.

The DM exchange vector  $\mathbf{D}$  vanishes when the symmetry of the crystal is high. This is the case, for example, when the point located halfway between the two magnetic ions in a unit cell is a center of inversion. In low-dimensional crystals where  $D \neq 0$ , the anisotropic exchange is typically the most important anisotropic contribution between spins. The DM interaction favors non-collinear spin configurations, with typical canted spins. As such, it determines the spin arrangements and it is responsible for the weak ferromagnetism observed in some predominantly antiferromagnetic crystals such as  $\alpha$ - $\text{Fe}_2\text{O}_3$ . The tendency toward canted spin configurations is most-easily seen by minimizing the energy in Eq. (4) for two classical spins, when the DM vector  $\mathbf{D}$  is, for example, perpendicular to the line joining the two ions. It can be shown that the minimum energy corresponds to a spin configuration where both spin are perpendicular to each other and to the direction of  $\mathbf{D}$ . Similar conclusions can be obtained by analyzing the same system quantum mechanically. The DM interactions is also responsible for proposed non-collinear spin configurations in magnetic clusters engineered by STM techniques on insulating surfaces.<sup>13,14</sup>

### B. The DM interaction for antiferromagnetic spin rings within a Hubbard model approach

In this section we specialize the previous discussion to the case of an antiferromagnetic spin triangle, and show how the DM interaction can be derived microscopically from a Hubbard model at half filling, in the presence of spin-orbit interaction.

As mentioned in the introduction, the low-energy magnetic properties of  $\{\text{Cu}_3\}$  are well-described by an isotropic antiferromagnetic Heisenberg model

$$H_{\text{H}} = \sum_{\langle i, j \rangle} J_{ij} \mathbf{s}_i \cdot \mathbf{s}_j, \quad J_{ij} > 0, \quad (5)$$

where  $\mathbf{s}_i$  are spin vector operators of magnitude  $s_i = 1/2$ , predominately localized at the three Cu sites. If the small distortion from a perfect equilateral arrangement of the three Cu atoms is neglected, the three exchange constants are the same,  $J_{ij} = J$ . DFT calculations<sup>7</sup> find  $J \approx 3.7$  meV. The GS manifold comprises two spin  $S = 1/2$  doublets, which can be represented by the two chiral states given in Eqs. (1), (2), or any two orthogonal linear combination of these. The spin  $S = 3/2$  excited-state multiplet is separated by the GS by an energy of order  $J$ .

It is well-known that the AFM Heisenberg model represents an effective low-energy spin model that can be derived from an underlying Hubbard model at half-filling in the large  $t/U$  limit. The choice of the best minimal model capturing the essential microscopic features of the electronic system is often a complex task, particularly when the exchange interaction between the magnetic ions is mediated via several paths involving non-magnetic ions, as for the case of  $\{\text{Cu}_3\}$ . We will neglect these complications and assume that an effective one-band Hubbard model suffices for this purpose. We will see that our first-principles calculations corroborate this choice, showing that one localized orbital at each magnetic ion indeed is enough to describe the low energy physics of the system. We will comment later on the possibility of considering a more complex Hubbard model to describe the non-magnetic bridges between Cu atoms, as well as the need of including more than one orbital at the Cu sites.

The second quantized one-band Hubbard Hamiltonian reads

$$H_U = -t \sum_{i,j} \sum_{\alpha} \left\{ c_{i\alpha}^{\dagger} c_{j\alpha} + \text{h.c.} \right\} + \frac{1}{2} U \sum_i n_{i\uparrow} n_{i\downarrow}, \quad (6)$$

where  $c_{i\alpha}^{\dagger}$  ( $c_{i\alpha}$ ) creates (destroys) an electron with spin  $\alpha$  at site  $i$  and  $n_{i\alpha} = c_{i\alpha}^{\dagger} c_{i\alpha}$  is the particle number operator. More precisely the index  $i$  labels a Wannier function localized at site  $i$ . The first term represents the kinetic energy, characterized by a spin-independent hopping parameter  $t$ , which is the same for all pairs of site due to the  $C_3$  symmetry of the  $\text{Cu}_3$  molecule magnet. The second-term is an on-site repulsion energy of strength  $U$ , which has an effect only when two electrons of opposite spins reside on the same site. It is the on-site repulsion energy.

The spin-orbit interaction in the Hubbard model is described by adding the following spin-dependent hopping term<sup>8,15–17</sup>

$$H_{\text{SOI}} = \sum_{i,j} \sum_{\alpha,\beta} \left\{ c_{i\alpha}^{\dagger} \left( i \frac{\mathbf{P}_{ij}}{2} \cdot \boldsymbol{\sigma}_{\alpha\beta} \right) c_{j\beta} + \text{h.c.} \right\}, \quad (7)$$

where  $\boldsymbol{\sigma}$  is the vector of the three Pauli matrices. Here the vector  $\mathbf{P}_{ij}$  is proportional to the matrix element of  $\nabla V \times \mathbf{p}$  between the orbital parts of the Wannier functions at sites  $i$  and  $j$ ;  $V$  is the one-electron potential and  $\mathbf{p}$  is the momentum operator. Clearly the spin-orbit term has the form of a spin-dependent hopping, which is added to the usual spin-independent hopping proportional to  $t$ . This form of the spin-orbit interaction is a special case of Moriya's hopping terms<sup>11</sup> in the limit that all but one orbital energy is taken to infinity.<sup>16</sup>

In contrast to the spin-independent hopping term, the spin-dependent hopping parameters are related by both the full symmetry of the molecule and the *local symmetry* of localized orbitals.<sup>8</sup> Now, because of the  $\sigma_v$  symmetry,  $\mathbf{P}_{ij} = P \mathbf{e}_z$ . The final expression of the Hubbard model, including the spin-orbit interaction is

$$H_{U+\text{SOI}} = \sum_{i,\alpha} \left\{ c_{i\alpha}^{\dagger} (-t + i\lambda_{\text{SOI}}\alpha) c_{i+1\alpha} + \text{h.c.} \right\} + \frac{1}{2} U \sum_i n_{i\uparrow} n_{i\downarrow}, \quad (8)$$

where  $\lambda_{\text{SOI}} \equiv P/2 = \mathbf{P}_{ij}/2 \cdot \mathbf{e}_z$  is the spin-orbit parameter.

We want to treat the two hopping terms perturbatively on the same footing, by doing an expansion around the atomic limit  $t/U$ ,  $\lambda_{\text{SOI}}/U \rightarrow 0$ . In many molecular magnets  $t \gg \lambda_{\text{SOI}}$ . This turns out to be the case also for  $\{\text{Cu}_3\}$ . In other molecules the two hopping parameters are of the same order of magnitude.

We are interested in the half-filling regime. We know that second-order perturbation theory in  $t$  results in an antiferromagnetic isotropic exchange term that splits the spin degeneracy of the low-energy sector of the Hubbard model, defined by the singly-occupied states. This action can be represented with an effective spin Hamiltonian, the isotropic Heisenberg model, with exchange constant  $J = 4t^2/|U|$ .<sup>18</sup> Similarly Loss *et al.* showed that another second-order term proportional to  $t\lambda_{\text{SOI}}/U$  generates an anisotropic exchange term that can be identified with the DM interaction.<sup>8</sup> They write approximate adapted many-body states to first-order in the perturbation  $|t|$ ,  $\lambda_{\text{SOI}} \ll U$ , corresponding to singly-occupied states. In particular there are two independent doublets,

$$|\psi_{E_{\pm}}^{1\alpha}\rangle = \frac{1}{\sqrt{3}} (|\downarrow\uparrow\uparrow\rangle + \epsilon_{\pm} |\uparrow\downarrow\uparrow\rangle + \epsilon_{\mp} |\uparrow\uparrow\downarrow\rangle), \quad (9)$$

and

$$|\psi_{E_{\pm}}^{1\alpha}\rangle = \frac{1}{\sqrt{3}} (|\uparrow\downarrow\downarrow\rangle + \epsilon_{\pm} |\downarrow\downarrow\uparrow\rangle + \epsilon_{\mp} |\downarrow\uparrow\downarrow\rangle), \quad (10)$$

with  $\epsilon_{\pm} = \exp(\pm 2\pi i/3)$ . These are states with  $S = 1/2$  and  $S_z = \pm 1/2$ . These states are formally identical to the chiral states given in Eqs. (1) and (2). Now, each of the terms appearing in these equations is a single Slater determinant obtained by three creation operators acting on the vacuum, e.g.,

$$|\uparrow\uparrow\downarrow\rangle \equiv c_{1\uparrow}^{\dagger} c_{2\uparrow}^{\dagger} c_{3\downarrow}^{\dagger} |0\rangle. \quad (11)$$

The states  $|\psi_{E'_+}^{1\alpha}\rangle$  and  $|\psi_{E'_-}^{1\alpha}\rangle$  are eigenstates of Hubbard Hamiltonian when  $t = \lambda_{\text{SOI}} = 0$ . The tunneling and SOI mix the singly-occupied and double-occupied states. The first-order correction is obtained by mixing in doubly-occupied states

$$|\Phi_{E'_\pm}^{1\alpha}\rangle \equiv |\psi_{E'_\pm}^{1\alpha}\rangle + \frac{(\epsilon_- - 1)(t \pm \alpha\lambda_{\text{SOI}})}{\sqrt{2}U} |\psi_{E'_\pm}^{2\alpha}\rangle + \frac{3\epsilon_+(t \pm \alpha\lambda_{\text{SOI}})}{\sqrt{2}U} |\psi_{E'_\pm}^{2\alpha}\rangle, \quad (12)$$

where

$$|\psi_{E'_\pm}^{2\alpha}\rangle = \frac{1}{\sqrt{6}} \sum_{i=1}^3 \epsilon_{1,2}^{i-1} (|\psi_{i1}^\alpha\rangle + |\psi_{i2}^\alpha\rangle), \quad (13)$$

and

$$|\psi_{E'_\pm}^{2\alpha}\rangle = \frac{1}{\sqrt{6}} \sum_{i=1}^3 \epsilon_{1,2}^{i-1} (|\psi_{i1}^\alpha\rangle - |\psi_{i2}^\alpha\rangle), \quad (14)$$

with  $|\psi_{ij}^\alpha\rangle = c_{i\uparrow}^\dagger c_{i\downarrow}^\dagger c_{j\alpha}^\dagger |0\rangle$  ( $i = 1, 2, 3$  and  $j \neq i$ ) representing the double-occupied sites.

The next step is to take the expectation value of the spin-orbit part of Eq.(8) in these approximated states. The result is<sup>8</sup>

$$\langle \Phi_{E'_\pm}^{1\alpha} | H_{\text{SOI}} | \Phi_{E'_\pm}^{1\alpha} \rangle = \pm \frac{5\sqrt{3}\lambda_{\text{SOI}}t}{2U} \text{sgn}(\alpha). \quad (15)$$

Note that off-diagonal matrix elements of  $H_{\text{SOI}}$  vanish; in other words, SOI splits but does not mix the chiral states.

In the small  $t/U$ ,  $\lambda_{\text{SOI}}/U$  limit, we can resort to a spin-only description of the low-energy physics of the system. The ground-state manifold (corresponding to the states Eq. (12)) is given by the two chiral spin states Eqs. (1), (2).

The anisotropic DM spin exchange Hamiltonian in  $D_{3h}$  symmetry is given by<sup>8</sup>

$$H_{\text{DM}} = \frac{iD_z}{2} \sum_1^3 (s_+^i s_-^{i+1} - s_-^i s_+^{i+1}) \quad (16)$$

Now, in the low energy regime corresponding to a  $D_{3h}$  symmetric molecule magnet, the spin-orbit interaction can be reduced to the effective form

$$H_{\text{SOI}} = \Delta_{\text{SOI}} C_z S_z, \quad (17)$$

where  $\Delta_{\text{SOI}}$  is the effective SOI coupling constant.

The DM interaction expressed in this form clearly shows that it splits but does not mix the two chiral states.<sup>28</sup> The splitting is exactly proportional to  $D_z$

and allows us, in the low-energy regime, to make the identification

$$D_z = \frac{5\lambda_{\text{SOI}}t}{U}. \quad (18)$$

This Hubbard model analysis suggests an avenue to extract the DM parameters from an ab-initio calculation. Only three parameters are needed, namely the spin-orbit interaction  $\lambda_{\text{SOI}}$ , the hopping parameter  $t$  and the on-site repulsion energy  $U$ .

### C. Semiclassical analysis of the DM interaction in frustrated spin systems

The quantum mechanical frustration present in an antiferromagnetic spin triangle and the DM interaction both tend to favor non-collinear spin configurations. It is instructive to study their interplay in a semiclassical approach, where non-collinearity is a more intuitive concept.

The *classical* Heisenberg model with energy functional given by Eq. (5) has two degenerate “ground states”, given by the two non-collinear spin configurations shown in Fig. 2. Classically these two states are the best way to by-pass the frustration present for any collinear spin configuration in a triangular antiferromagnet. Quantum mechanically the two non-collinear spin configurations can be represented by the states

$$|\psi_{\text{nc}\pm}\rangle = \left[ (\alpha_1|\uparrow\rangle_1 + \beta_1|\downarrow\rangle_1) \otimes (\alpha_2|\uparrow\rangle_2 + \beta_2|\downarrow\rangle_2) \otimes (\alpha_3|\uparrow\rangle_3 + \beta_3|\downarrow\rangle_3) \right], \quad (19)$$

where  $\alpha = \cos(\theta/2)$  and  $\beta = \exp\{i\phi\} \sin(\theta/2)$ . Here  $\theta$  is the elevation angle and  $\phi$  is the azimuth angle. The three spinors  $(\alpha_i|\uparrow\rangle_i + \beta_i|\downarrow\rangle_i)$ ,  $i = 1, 2, 3$  are three spin-1/2 coherent states defined by the three non-collinear directions obtained by rotating consecutively by the angle  $\pm 240^\circ$  (see Fig. 2). Anticlockwise rotations (by  $-240^\circ$ ) define a left-handed helical state (Fig. 2(a)); clockwise rotations (by  $+240^\circ$ ) define a right-hand helical state (Fig. 2(b)).

In contrast to the true GS given in Eqs. (1), (2) the non-collinear states defined in Eq. (19) are neither eigenstates of the quantum Hamiltonian Eq. (5) nor of  $\mathbf{S}^2$  and  $S_z$ . The expectation value of the Hamiltonian  $H_H$  at these states is defined by

$$\langle \psi_{\text{nc}\pm} | H_H | \psi_{\text{nc}\pm} \rangle = 3J/4. \quad (20)$$

The fact that the energy of the collinear states is higher than the energy of the chiral states by  $3J/8$  is not surprising, since the noncollinear states defined



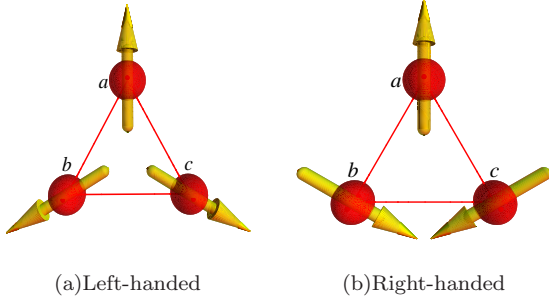


FIG. 2: Non-collinear helical system of three Cu-atom spins. Anticlockwise rotations (by  $-240^\circ$ ) define a left-handed helical state (a); clockwise rotations (by  $+240^\circ$ ) define a right-hand helical state (b).

in Eq. (19) are a mixture of  $S = 1/2$  and  $S = 3/2$  components.

When rewritten in term of the electronic states for the corresponding Hubbard model at half-filling in the small  $t/U$  limit, the non-collinear spin-coherent states defined in Eq. (19) can be considered to be the “best” energy states given by a single Slater determinant (Note that the chiral states cannot be written as a single Slater determinant).

It is now interesting to examine the effect of the DM interaction on these states. A straightforward calculations shows that for the DM interaction of Eq. (16), where only the  $z$ -component of  $\mathbf{D}$  is nonzero

$$\langle \psi_{\text{nc} \pm} | H_{\text{DM}} | \psi_{\text{nc} \pm} \rangle = \pm \frac{3\sqrt{3}}{4} D_z. \quad (21)$$

Therefore, as for the GS manifold of the exact eigenstates, the DM interaction *splits* but does *not couple* the two noncollinear states. The DM parameter  $D_z$  is, by Eq. (21), related to the DM interaction-induced energy-gap between the two noncollinear states

$$\begin{aligned} \Delta E_{\text{nc}} &= \langle \psi_{\text{nc}+} | H_{\text{DM}} | \psi_{\text{nc}+} \rangle - \langle \psi_{\text{nc}-} | H_{\text{DM}} | \psi_{\text{nc}-} \rangle \\ &= \frac{3\sqrt{3}}{4} D_z. \end{aligned} \quad (22)$$

This result suggests a way of extracting the DM vector parameter  $\mathbf{D}$  similar in spirit to the method used to calculate the isotropic exchange parameter  $J$  by comparing the energy difference of states with ferromagnetic and antiferromagnetic spin configurations respectively. In the next section we will see that this procedure can also be carried out by first-principle methods.

### III. AB-INITIO CALCULATION OF THE DM VECTOR

All the calculations in this work are carried out by using *ab initio* package NRLMOL<sup>19,20</sup>, which uses a Gaussian basis set to solve the Kohn-Sham equations within PBE-GGA approximation.<sup>21</sup> For more computational details and the electronic properties of  $\{\text{Cu}_3\}$  we refer the reader to our previous work.<sup>7</sup>

#### A. Calculation of the hopping term $t$

As discussed in the section IIB, the Hubbard model approach is based on allowing the localized electrons to hop to its nearest neighbor sites and in the present case of the  $\{\text{Cu}_3\}$  molecule, these localized electrons are  $d$  electrons. Therefore, for calculating hopping parameter  $t$ , the relevant states are those  $d$  electron states that lie close to the Fermi level. Let  $|K, \alpha\rangle$  be the three relevant Kohn-Sham eigenstates calculated from NRLMOL. We can write them as a linear combination of the localized atomic orbitals, centered at the three Cu sites,  $\{|\phi_a\rangle, |\phi_b\rangle, |\phi_c\rangle\} \otimes |\chi_\alpha\rangle$ , with  $\alpha = \uparrow, \downarrow$  for spin up and down, respectively:

$$|K, \alpha\rangle = \sum_i C_{K\alpha}^i |\phi_i\rangle |\chi_\alpha\rangle. \quad (23)$$

where  $C_{K\alpha}^i$  is the weight of the localized  $|\phi_i\rangle |\chi_\alpha\rangle$  wavefunction.

For the  $|\uparrow\uparrow\uparrow\rangle$  spin configuration, in the absence of spin-orbit interaction, the relevant three levels around the Fermi level are doubly and singly degenerate. These levels are sketched in Fig. 3

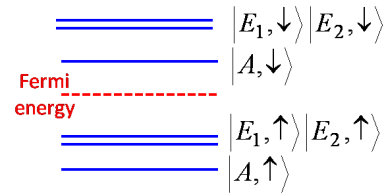


FIG. 3: Schematic diagram of the Kohn-Sham energy levels around the Fermi level

We obtain the level structure by diagonalizing the three-site Hamiltonian in the absence of the SOI:

$$H_0 = \varepsilon_0 \sum_i |\phi_i\rangle \langle \phi_i| - t \sum_{i \neq j} |\phi_i\rangle \langle \phi_j|, \quad (24)$$

where  $\varepsilon_0$  is the onsite energy,  $t$  is the hopping term and  $i, j = a, b, c$  represent the copper sites. We get

the eigenvalues  $\varepsilon_0 + t$  and  $\varepsilon_0 - 2t$  for the two-fold and one-fold degenerate states, respectively. The Kohn-Sham eigenvectors can be defined as a linear combination of the localized wavefunctions,

$$\begin{aligned} |E_1, \uparrow\rangle &= \frac{1}{\sqrt{2}} (|\phi_a\rangle - |\phi_b\rangle) |\uparrow\rangle, \\ |E_2, \uparrow\rangle &= \frac{1}{\sqrt{6}} (|\phi_a\rangle + |\phi_b\rangle - 2|\phi_c\rangle) |\uparrow\rangle, \\ |A, \uparrow\rangle &= \frac{1}{\sqrt{3}} (|\phi_a\rangle + |\phi_b\rangle + |\phi_c\rangle) |\uparrow\rangle. \end{aligned} \quad (25)$$

Now the localized states can be written in term of the Kohn-Sham functions

$$\begin{aligned} |\phi_a\rangle |\uparrow\rangle &= \frac{|A, \uparrow\rangle}{\sqrt{3}} + \frac{|E_1, \uparrow\rangle}{\sqrt{2}} + \frac{|E_2, \uparrow\rangle}{\sqrt{6}}, \\ |\phi_b\rangle |\uparrow\rangle &= \frac{|A, \uparrow\rangle}{\sqrt{3}} - \frac{|E_1, \uparrow\rangle}{\sqrt{2}} + \frac{|E_2, \uparrow\rangle}{\sqrt{6}}, \\ |\phi_c\rangle |\uparrow\rangle &= \frac{|A, \uparrow\rangle}{\sqrt{3}} - 2\frac{|E_2, \uparrow\rangle}{\sqrt{6}}. \end{aligned} \quad (26)$$

Our calculations showed that these states are primarily localized on the Cu atoms and have  $d$  character. We have obtained the Kohn-Sham eigenenergies for the one-fold and two-fold degenerate states

$$\begin{aligned} \langle E_1, \uparrow | H_0 | E_1, \uparrow \rangle &= \frac{1}{2} (\langle \phi_a | - \langle \phi_b |) H_0 (|\phi_a\rangle - |\phi_b\rangle) \\ &= \varepsilon_0 + t, \\ \langle A, \uparrow | H_0 | A, \uparrow \rangle &= \frac{1}{3} (\langle \phi_a | + \langle \phi_b | + \langle \phi_c |) H_0 \\ &\quad (|\phi_a\rangle + |\phi_b\rangle + |\phi_c\rangle) \\ &= \varepsilon_0 - 2t. \end{aligned} \quad (27)$$

From Eqs. (27) we can finally evaluate the value of the parameter  $t$  as:

$$\begin{aligned} t &= \frac{1}{3} (\langle E_1, \uparrow | H_0 | E_1, \uparrow \rangle - \langle A, \uparrow | H_0 | A, \uparrow \rangle) \\ &= 50.84 \text{ meV}. \end{aligned} \quad (28)$$

### B. Calculation of the spin-orbit interaction parameter $\lambda_{SOI}$

Standard spin-orbit interaction representation for spherical systems is given by

$$U_{so}(r, \mathbf{L}, \mathbf{S}) = \frac{1}{2c^2} \mathbf{S} \cdot \mathbf{L} \frac{1}{r} \frac{d\Phi(r)}{dr}, \quad (29)$$

where  $r$  is the position,  $\mathbf{L}$  is the angular momentum,  $\mathbf{S}$  is the spin moment,  $c$  is the speed of light, and  $\Phi$  is a spherically symmetric potential. The above equation is exact for spherical systems. For a multicenter system a superposition of such terms needs to be

considered. However, this approximation could miss non-spherical correlations important for anisotropic energies. Instead of using Eq. (29), a generalization of the spin-orbit interaction for non-spherical or multicenter systems is given by

$$U_{so}(\mathbf{r}, \mathbf{p}, \mathbf{S}) = -\frac{1}{2c^2} \mathbf{S} \cdot \mathbf{p} \times \nabla \Phi(\mathbf{r}), \quad (30)$$

where  $\mathbf{p}$  is the momentum operator and a external electric field is given by  $\mathbf{E} = -\nabla \Phi$ .

Pederson *et. al* (see Ref. 22) have shown an exact simplified method for incorporating spin-orbit coupling into density-functional calculations. In order to get the basis-set for the spin-orbit coupling the single-electron wave function can be expressed as

$$\psi_{is}(\mathbf{r}) = \sum_{j\alpha} C_{j\alpha}^{is} f_j(\mathbf{r}) \chi_\alpha, \quad (31)$$

where  $f_j(\mathbf{r})$  is a spatial basis function,  $\chi_\alpha$  is either a majority or minority spin spinor, and  $C_{j\alpha}^{is}$  are determined by effectively diagonalizing the Hamiltonian matrix. In order to calculate the effect of the SOI (Eq. (30)) it is necessary to calculate matrix elements of the form

$$\begin{aligned} U_{j\alpha, k\alpha'} &= \langle f_j \chi_\alpha | U(\mathbf{r}, \mathbf{p}, \mathbf{S}) | f_k \chi_{\alpha'} \rangle \\ &= \sum_x \frac{1}{i} \langle f_j | V_x | f_k \rangle \langle \chi_\alpha | S_x | \chi_{\alpha'} \rangle, \end{aligned} \quad (32)$$

where

$$\langle f_j | V_x | f_k \rangle = \frac{1}{2c^2} \left( \left\langle \frac{df_j}{dz} \middle| \Phi \right| \frac{df_k}{dy} \right\rangle - \left\langle \frac{df_j}{dy} \middle| \Phi \right| \frac{df_k}{dz} \right\rangle. \quad (33)$$

The matrix elements for  $V_y$  and  $V_z$  are obtained by cyclical permutations of  $x, y$  and  $z$  in Eq. (33). This methodology for the SOI matrix gives several advantages, namely, it does not require the determination of the electric field; it is specially ideal for basis functions constructed from Gaussian-type orbitals, Slater-type functions, and plane waves.

We are interested in the matrix elements in the localized basis-set, Eq. (26):

$$\begin{aligned} \langle \phi_i | \langle \chi_\uparrow | U_{so} | \phi_k \rangle | \chi_\uparrow \rangle &= -\frac{1}{2c^2} \langle \phi_i | \mathbf{p} \times \nabla \Phi(\mathbf{r}) | \phi_k \rangle \\ &\quad \cdot \langle \chi_\uparrow | \mathbf{S} | \chi_\uparrow \rangle \\ &= \frac{1}{2i} \langle \phi_i | V_z | \phi_k \rangle \\ &= -\frac{i}{2} p_{ik}^z \equiv -i\lambda_{SOI}. \end{aligned} \quad (34)$$

We can write these matrix elements in the Kohn-Sham basis set

$$\begin{aligned} \langle \phi_i | \langle \chi_\uparrow | U_{so} | \phi_k \rangle | \chi_\uparrow \rangle &= \sum_{KK'} (\tilde{C}_{K\uparrow}^i)^* \tilde{C}_{K'\uparrow}^k \\ &\quad \times \langle K, \uparrow | U_{SOI} | K', \uparrow \rangle \end{aligned} \quad (35)$$

We have obtained the matrix elements for the spin-orbit interaction in the Kohn-Sham basis,  $\{|E_1\rangle, |E_2\rangle, |A\rangle\} \otimes |\chi_\alpha\rangle$  (Eq. (35)), and used Eqs. (26) to obtain the matrix elements:

$$p^z = \begin{pmatrix} 0 & 0.85 & 0.85 \\ 0.85 & 0 & 0.85 \\ 0.85 & 0.85 & 0 \end{pmatrix}. \quad (36)$$

From Eq. (34) we have  $\lambda_{SOI} = p_{ik}^z/2 = 0.43$  meV.

### C. Calculation of the Hubbard $U$ and evaluation of $D_z$ and $J$

The most common approach for calculating  $U$  involves calculation of energy,  $E$ , of the molecule with  $N$ ,  $N+1$  and  $N-1$  electron and extracting  $U$  from the equation below,

$$\begin{aligned} U &= E(N+1) + E(N-1) - 2E(N) \\ &= [E(N+1) - E(N)] - [E(N) - E(N-1)] \\ &= A - I. \end{aligned} \quad (37)$$

In the above equation  $A$  is (minus) the electron affinity<sup>29</sup> and  $I$  is the ionization energy. For systems that are not closed shell, such as those considered here, the  $U$  value is essentially the second derivative of energy with respect to charge and it is possible to determine  $U$  by calculating the energy as a function of charge.

For the single-band Hubbard-model corresponding to the  $\{\text{Cu}_3\}$  molecule, we are interested in obtaining energies for the charge-transfer excitations involving the transfer of a localized  $d$ -electron on one copper site to a localized  $d$ -electron on another site. Specifically we wish to know the energy of  $|X\rangle = |\uparrow_a \downarrow_a \uparrow_c\rangle$  relative to  $|\uparrow_a \downarrow_b \uparrow_c\rangle$ . There are a total of twelve charge-transfer excitations that can be made with one-site doubly occupied and one electron on one of the other sites. For the half-filled case of interest here, the energy difference depends upon the electron affinity of the state on site  $a$ , the ionization energy of the state on site  $b$  and the residual long-range coulomb interaction between the negatively charged electron added to site  $a$  and the positively charged hole that is left behind on site  $b$ . Since site  $b$  and site  $a$  are equivalent, it follows that we simply need to calculate  $U$  for any one of the copper sites in the half filled case. A very rough estimate of the charge transfer energy may be determined by calculating the PBE-GGA energy of the Cu atom with an electron configuration of  $1s^2 2s^2 3s^2 4s^2 p^6 3d^n$  with  $n=8,9,10$ . Using  $n=9$  as the reference state, one finds a bare  $U$  value

of 13.76 eV which, after accounting for the particle-hole interaction ( $27.2116/R_{\text{Cu}-\text{Cu}} = 2.95$  eV, where  $R_{\text{Cu}-\text{Cu}} = 4.87$  Bohr is the distance between magnetic centers) is shifted to 10.8 eV.

In the  $\{\text{Cu}_3\}$  molecule, we have chosen to calculate  $U$  quasi-analytically by gradually adding (or subtracting) a small fraction of electronic charge  $\delta q$  to one of the half-filled Cu  $d$ -states. The energy of the system as a function of  $\delta q$  is shown in Fig. 4, where we can see that it can well be reproduced by a quadratic fitting curve. The figure shows that, upon adding a fractional charge to a localized orbital, the total energy initially decreases, since the orbital energy is negative. Eventually, however, the competing Coulomb repulsion takes over and the net change in total energy for adding one electron to a localized orbital is positive. In contrast, with one extra electron delocalized throughout the molecule the total energy is usually smaller than the energy of the neutral molecule.

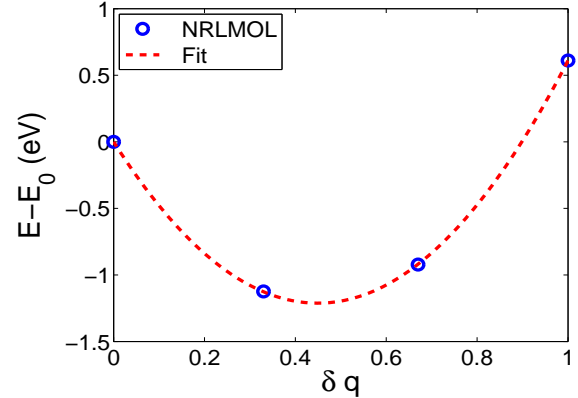


FIG. 4: (Color online) Dependence of the total energy on added fractional charge  $\delta q$ . The (blue) circle represent the results of NRLMOL calculations and the dashed (red) line represents a quadratic fit.

The difference in the energy of the system before and after adding a fraction of electronic charge  $\delta q$  is given by  $\Delta E = U_{eff} = U\delta q^2 - e^2\delta q^2/R_{\text{Cu}-\text{Cu}}$ , where  $U = \partial^2 E(q)/\partial q^2$ . We have calculated the effective parameter  $U_{eff}$  by setting  $\delta q = 1$ :

$$\begin{aligned} U_{eff} &= \delta q^2 \left( \frac{\partial^2 E(q)}{\partial q^2} - \frac{e^2}{R_{\text{Cu}-\text{Cu}}} \right) \\ &= 9.06 \text{ eV}, \end{aligned} \quad (38)$$

where  $E(q) = E_0 + (U/2)(q - q_0)^2$  with  $E_0$  being a constant.



### 1. Evaluation of $D_z$ and $J$

Having calculated the parameters  $t$ ,  $\lambda_{SO}$ , and  $U_{eff}$ , we are now able to use Eq. (18) and evaluate the Dzyaloshinskii-Moriya parameter  $D_z$ . We obtain

$$D_z = 5 \frac{\lambda_{SO} t}{U_{eff}} = 0.01 \text{ meV}. \quad (39)$$

This value of  $D_z$  yields a small splitting of the chiral state,  $\Delta \approx 0.02 \text{ meV} \approx 0.3 \text{ K}$ . Experimental estimates of the DM parameter find a splitting 3-4 times larger than this value. Considering the smallness of this energy and the uncertainty in the experimental measurements, the two estimates are consistent with each other. On the other hand, it is also possible that part of the discrepancy between theory and experiment is due to the fact that other mechanisms, different from the DM interaction, contribute to the splitting. In particular Ref.<sup>23</sup> pointed out that small deformations of the triangular molecule can lift the chiral degeneracy and this contribution to the splitting could be even more important than the DM interaction. If this is indeed the case, our results would imply that our method of computing the DM parameter is actually rather accurate.

From a computational point of view, it is interesting at this point to evaluate the isotropic exchange constant  $J$  from the Hubbard model perturbative approach, which gives

$$J = 4t^2/U \approx 1 \text{ meV}. \quad (40)$$

This estimate of  $J$  is considerably closer to the experimental value of  $0.5 \text{ meV}$  than the value of  $3.7 \text{ meV}$  obtained by computing the energy difference between states with ferromagnetic and antiferromagnetic spin configurations.<sup>7</sup>

### D. Comparison with other methods

In a recent work Takeda *et al.*<sup>24</sup> have used a non-collinear approach to estimate the DM interaction. Instead of the use of simple product functions, this work capitalizes on the use of generalized orbitals which are composed of a linear combination of both spinors with different and variable spatial functions. By using such a representation it is possible to develop single-determinants which are composed of a linear combination of the chiral spin  $1/2$  states and the non-chiral spin  $3/2$  states. For

example, the states associated with the system depicted in Fig 2(a) would be represented according to:

$$\begin{aligned} |\psi_{nc\pm}\rangle &= |X_{\pm}^a X_{\pm}^b X_{\pm}^c\rangle \\ &= \frac{1}{2\sqrt{2}} \left( |\uparrow\uparrow\uparrow\rangle \pm i |\downarrow\uparrow\uparrow\rangle \mp (-1)^{1/6} |\uparrow\downarrow\uparrow\rangle \right. \\ &\quad \mp (-1)^{5/6} |\uparrow\uparrow\downarrow\rangle \mp i |\downarrow\downarrow\downarrow\rangle - |\uparrow\downarrow\downarrow\rangle \\ &\quad \left. + (-1)^{1/3} |\downarrow\uparrow\downarrow\rangle - (-1)^{2/3} |\downarrow\downarrow\uparrow\rangle \right) \end{aligned} \quad (41)$$

where  $X_+(\theta, \phi) = \cos(\theta/2) |\uparrow\rangle + \exp\{i\phi\} \sin(\theta/2) |\downarrow\rangle$  and  $X_-(\theta, \phi) = \sin(\theta/2) |\uparrow\rangle - \exp\{i\phi\} \cos(\theta/2) |\downarrow\rangle$ , with  $\theta = \pi/2$  and  $\phi = \pi/2, 7\pi/2, -\pi/2$ . They further claim that  $\Delta E_{nc} = 3\sqrt{3}/4D_z$  (see Eq. 22) can be estimated by a perturbational treatment of the SOI, as follows

$$\Delta E_{nc} = \langle \psi_{nc+} | H_{SOI} | \psi_{nc+} \rangle - \langle \psi_{nc-} | H_{SOI} | \psi_{nc-} \rangle, \quad (42)$$

where  $H_{SOI}$  is the one-electron spin-orbit interaction. These expectation values can be calculated by DFT.

It is clear from the expression Eq. (41) that the expectation value of the spin-orbit interaction for this and other states would be linear so, without other considerations, one can not extract an interaction that depends upon the excitations of interest to the Hubbard Hamiltonian. However, in analogy to the expansion of the many-electron wavefunction for molecular hydrogen in regions intermediate between the bonding and separated-atom limit, a self-consistent optimization of such a starting determinant allows the spin-orbitals to be intermediate between the doubly occupied and single occupied representations. While the resulting noncollinear wavefunction is still a single Slater determinant in character, expansion of the noncollinear state in terms of the Hubbard states would show a wavefunction comprised primarily of the  $8 \times 8$  half-filled determinants but would also contain small contributions of the ionic contributions which are shifted upward by  $U_{eff}$ . It is the small admixture of these states that allow Takeda *et al.* to extract both the exchange parameters and the DM interaction through the use of noncollinear representations. This approach could have advantages from an operational viewpoint since it effectively addresses the potential role of other excited states that are routinely excluded from the Hubbard Hamiltonian. However, the precise interactions which ultimately mediate the appearance of the DM interaction require additional analysis which is every bit as arduous as that presented here.

An alternative method to calculate the DM vector, based on Andersen's "local force theorem"<sup>25</sup>,

was developed by Solovyev *et al.*<sup>26</sup> More recently this method was utilized in conjunction with DFT to study the DM interaction between magnetic atoms inserted in different crystalline systems and surfaces.<sup>14,27</sup> Essentially this method expresses the DM vector in terms of the Green's functions of the system, modified by the spin-orbit interaction. Although computationally sophisticated, the Green's function method is physically less transparent than the one adopted here, particularly for a finite system such a triangular SMM, where the crucial ingredients leading to the anisotropic DM exchange can be reduced to a few parameters that have a direct physical interpretation within the Hubbard model.

#### IV. CONCLUSIONS

We carried out a first-principles investigation of the zero-field splitting of the chiral ground states of a  $\{\text{Cu}_3\}$  single-molecule magnet (SMM), caused by the Dzyaloshinskii-Moriya interaction. Our approach relies on the perturbative analysis of a Hubbard model, which includes spin-orbit interaction. In the large  $U$  limit, appropriate for  $\{\text{Cu}_3\}$ , it is possible to express the Dzyaloshinskii-Moriya constant in terms of the parameters that define the Hubbard model, such as the effective hopping integral between magnetic sites  $t$ , the on-site repulsion energy  $U$ , and the strength of the spin-orbit  $\lambda_{\text{SOI}}$ . We then carried out an approximate method to extract the values of these parameters from our spin density functional theory calculations of the SMM. The value of the Dzyaloshinskii-Moriya constant  $D$  that we found is of the order of 0.01 meV, which is a factor of 5 smaller than the value measured experimentally. Given the uncertainty of the experimental result and the fact that other effects might contribute to the zero-field spin splitting of the chiral

states, our estimate should be considered consistent with experiment.

The method of computing the DM parameter by effectively extending Anderson's theory of superexchange to include spin-orbit interaction is very close to Moriya's original formulation of anisotropic exchange. It is interesting to note that if we use this approach to calculate the isotropic superexchange constant  $J$  of the Heisenberg model describing  $\{\text{Cu}_3\}$ , we obtain a value that is closer to experimental result than the estimates based on total energy calculations of ferromagnetic vs antiferromagnetic spin configurations. This seems to suggest that this approach is not only physically very intuitive, but it might also bear promise of good numerical accuracy.

While the methods discussed here provide physical insight into the nature of the DM interaction, we note that for future calculations it would be desirable to consider excitations that are not normally included in the single-band Hubbard model. For such an approach it would be necessary to include methodologies that allow for the calculation of all excitations in such systems.

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- <sup>28</sup> Note also that the Hamiltonian in Eq. 16 does not mix the GS spin  $S = 1/2$  manifold with the excited-state spin  $S = 3/2$  multiplet and leaves the latter unchanged.
- <sup>29</sup> Note that usually, the electron affinity is defined as  $[E(N) - E(N + 1)]$ , where  $E(N)$  is the energy of the neutral system.